

CONTROL OF CELL SWELLING

BY THE PROPER CHOICE OF CARBON MONOFLUORIDE (CF_x)
5 CATHODE MATERIALS IN HIGH RATE DEFIBRILLATOR CELLS

CROSS-REFERENCE TO RELATED APPLICATION

The present application claims priority based on
10 provisional application Serial No. 60/205,361, filed
May 18, 2000.

BACKGROUND OF THE INVENTION

1. Field of Invention

15 The present invention generally relates to the
conversion of chemical energy to electrical energy.
More particularly, the present invention is directed to
the use of carbon monofluoride (CF_x) in high pulse power
cells containing a transition metal oxide such as silver
20 vanadium oxide (SVO).

It has been discovered that when CF_x material is
prepared from highly structured carbon precursors, cell
swelling during high current pulse discharge conditions
is markedly reduced, and in some cases eliminated.
25 Still more particularly, the present invention describes
a lithium electrochemical cell designed for high rate
discharge applications in which the cathode electrode
preferably has a sandwich design of the configuration:
SVO/current collector/ CF_x /current collector/SVO. Cells
30 with this cathode electrode design are particularly
applicable for powering implantable medical devices,
such as cardiac defibrillators, requiring a relatively
low electrical current for device monitoring functions
interrupted from time to time by a high current pulse
35 discharge for device activation.

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Other than cell capacity, an important consideration for an implantable medical device application is cell swelling during discharge. In order to prevent damage to device circuitry, enough void space must be left inside the powered device to accommodate this volume change. The more cell swelling, the more

void space that must be reserved. Cell swelling, therefore, impacts the device total volume. In the field of implantable biomedical devices, a smaller total device volume is desired. Thus, in order to provide a more compact device design, it is desirable to minimize or eliminate cell swelling. Excessive cell swelling is also detrimental to the proper functioning of the implantable medical device and, consequently, to its safe use.

Carbon monofluoride, CF_x is a cathode active material that has found wide spread use for low-weight lithium cells. In fact, Li/CF_x cells are particularly useful for discharge applications requiring relatively low currents of about 1 microamperes to about 100 milliamperes. At these discharge rates, cell swelling is generally not observed. However, when Li/CF_x cells having the cathode active material synthesized from petroleum coke are discharged under relatively high current applications, i.e., from about 15.0 mA/cm² to about 35.0 mA/cm², significant cell swelling is observed.

Cells powering implantable cardiac defibrillators are periodically pulse discharged under very high current densities of 15.0 mA/cm² and higher. Therefore, when CF_x is included in a sandwich cathode design as part of an electrode assembly powering an implantable medical device, such as a cardiac defibrillator, and the active material is synthesized from certain carbonaceous precursors such as petroleum coke, a potential cell swelling problem exists.

Accordingly, what is needed is a fluorinated carbon active material which is capable of being subjected to relatively high rate discharge conditions without appreciably swelling. Such a material would be very

desirable for inclusion into a high rate cell powering an implantable medical device.

SUMMARY OF THE INVENTION

5 According to the present invention, the swelling of cells containing sandwich cathodes, such as of a SVO/CF_x/SVO configuration, is significantly minimized by using a CF_x material synthesized from carbon fibers, and mesophase carbon microbeads (MCMB). These carbonaceous
10 materials are identified as those which result in the least amount of swelling in cells containing CF_x as part of the cathode material relative to those synthesized from graphite or petroleum coke. This is especially important when the cell is being pulse discharged.

15 These and other aspects of the present invention
will become increasingly more apparent to those skilled
in the art by reference to the following description and
the appended drawing.

20 BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic view of carbon fibers having an annual ring layered structure according to the present invention.

Fig. 2 is a cross-sectional view along line 2-2 of
25 Fig. 1.

Fig. 3 is a schematic view of carbon fibers having a radial layered structure according to the present invention.

Fig. 4 is a cross-sectional view along line 4-4 of
30 Fig. 3.

Fig. 5 is a schematic view of mesophase carbon microbeads with a radial-like structure according to the present invention.

Fig. 6 is a cross-sectional view along line 6-6 of Fig. 5.

Fig. 7 is a scanning electron microscope photograph of standard CF_x synthesized from petroleum coke having a plate like morphology.

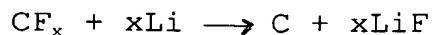
Fig. 8 is a scanning electron microscope photograph of CF_x synthesized from a fibrous carbon material according to the present invention.

Fig. 9 is a graph of cell thickness versus depth of discharge for a prior art cell having CF_x synthesized from petroleum coke in comparison to a present invention cell having CF_x synthesized from carbon fiber.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to minimization and even elimination of swelling in lithium cells containing CF_x as part of the cathode electrode and discharged under high rate applications. This improvement in cell functionality results from CF_x materials being synthesized from carbonaceous precursors having special structural characteristics. Preferred precursors are carbon fibers and MCMB. During discharge, and especially during high rate discharge, these CF_x materials retain the layered structure of the carbonaceous precursor.

Upon being discharged in lithium cells, lithium ions intercalate into the layered carbonaceous structure to react with fluorine, which is attached to the carbon backbone either covalently or ionically. This forms lithium fluoride and the reaction is shown below:



It is well known that lithium ions exist in the electrolyte mostly as solvent solvated ions. When lithium ions intercalate into the carbon layers of CF_x during discharge, solvent co-intercalation is also thought to occur. It is hypothesized that the co-intercalated solvent molecules form a solvated reaction intermediate. This intermediate causes destruction of the carbon structure and results in expansion of the discharged CF_x active material. During high rate discharge conditions, a greater amount of solvent molecules co-intercalate into the layered carbonaceous structure within a shorter period of time. Such rapid co-intercalation creates a relatively high concentration of solvent molecules locally which, in turn, causes destruction or expansion of the layered structure at the local region. Therefore, in order to minimize or eliminate cell swelling, destruction or expansion of the layered carbonaceous structure due to solvent co-intercalation needs to be minimized.

Minimization of carbonaceous structure destruction due to co-intercalation is achieved by carefully selecting the microstructure of the carbonaceous precursor materials. In that respect, various carbon fiber materials are suitable for synthesizing CF_x active materials. For example, Figs. 1 and 2 show a schematic of carbon fibers 10 having annual ring layers 12 where graphite crystallite edges are exposed only on the cross section. Figs. 3 and 4 show a schematic of carbon fibers 20 with radial layers 22 where the entire fiber surface has the graphite crystallite edges 24 exposed. Figs. 5 and 6 show a schematic of a MCMB 30 with a radial-like texture where the entire surface of the microbead has exposed graphite crystallite edges 32.

CF_x material synthesized from carbon fibers exhibit a markedly different morphology than standard CF_x material synthesized from petroleum coke. When imaged using a scanning electron microscope at 1000x, the standard material displays a plate like morphology (Fig. 7), whereas the present invention material displays a fiber like morphology (Fig. 8). The difference between the materials is also reflected in the five point BET surface area. The surface area of CF_x synthesized from petroleum coke is about 155 m²/g, whereas the surface area of CF_x synthesized from fibrous materials according to the present invention ranges from about 295 m²/g to about 346 m²/g. The prior art CF_x material has a mean particle size, by volume %, of about 16.47 μm, whereas the particle size for the fiber material ranges, by volume %, from about 4.37 μm to about 6.92 μm. A thermogravimetric/differential thermal analysis (TGA/DTA) was simultaneously conducted on both materials under a flowing argon atmosphere at a rate of 20°C from room temperature to 750°C, and the results are set forth below in Table 1.

Table 1

Parameter	standard CF _x	fiber CF _x
BET surface area (m ² /g)	155	295-346
particle size volume % (μm)	16.5	4.37-6.92
particle size surface area %	3.97	1.71-2.12
particle size number %	0.716	0.642- 0.686
DTA exotherm (°C)	667	652-656
min TGA % weight loss to 750°C	79.5	75.7
max TGA % weight loss to 750°C	83.7	83.7

In the case of carbon fibers and MCMB with radial like structures, solvent co-intercalation expansion of the carbonaceous materials is expected to be small due to the physical restraint of the carbon layered structure. When solvent molecules intercalate into the carbon layers of these materials, the increased d_{002} spacing between the graphite layers generates expansion tension parallel to the carbon surface. Thus, unless the three dimensional structure of the MCMB carbon fibers breaks apart, the carbon particles are unlikely to swell. As a result, the cell swelling phenomenon is minimized.

In general, any carbonaceous material with a structure which restricts an increase in the d_{002} spacing between graphite layers is considered a good precursor for CF_x synthesis according to the present invention. Accordingly, the use of CF_x synthesized from these carbon materials is beneficial to minimize or eliminate cell swelling.

An electrochemical cell that possesses sufficient energy density and discharge capacity required to meet the vigorous requirements of implantable medical devices comprises an anode of a metal selected from Groups IA, IIA and IIIB of the Periodic Table of the Elements. Such anode active materials include lithium, sodium, potassium, etc., and their alloys and intermetallic compounds including, for example, Li-Si, Li-Al, Li-B and Li-Si-B alloys and intermetallic compounds. The preferred anode comprises lithium. An alternate anode comprises a lithium alloy such as a lithium-aluminum alloy. The greater the amount of aluminum present by weight in the alloy, however, the lower the energy density of the cell.

The form of the anode may vary, but preferably the anode is a thin metal sheet or foil of the anode metal, pressed or rolled on a metallic anode current collector, i.e., preferably comprising titanium, titanium alloy or nickel, to form an anode component. Copper, tungsten and tantalum are also suitable materials for the anode current collector. In an exemplary cell according to the present invention, the anode component has an extended tab or lead of the same material as the anode current collector, i.e., preferably nickel or titanium, integrally formed therewith such as by welding and

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y = 5.8, γ -phase silver vanadium oxide having in the general formula $x = 0.80$ and $y = 5.40$ and ϵ -phase silver vanadium oxide having in the general formula $x = 1.0$ and $y = 5.5$, and combination and mixtures of phases thereof.

5 For a more detailed description of such cathode active materials reference is made to U.S. Patent No. 4,310,609 to Liang et al., which is assigned to the assignee of the present invention and incorporated herein by reference.

Another preferred composite transition metal oxide
10 cathode material includes V_2O_z wherein $z \leq 5$ is combined with Ag_2O with silver in either the silver(II), silver(I) or silver(0) oxidation state and CuO with copper in either the copper(II), copper(I) or copper(0) oxidation state to provide the mixed metal oxide having the general
15 formula $Cu_xAg_yV_2O_z$, (CSVO). Thus, the composite cathode active material may be described as a metal oxide-metal oxide-metal oxide, a metal-metal oxide-metal oxide, or a metal-metal-metal oxide and the range of material composition found for $Cu_xAg_yV_2O_z$ is preferably about 0.01
20 $\leq z \leq 6.5$. Typical forms of CSVO are $Cu_{0.16}Ag_{0.67}V_2O_z$ with z being about 5.5 and $Cu_{0.5}Ag_{0.5}V_2O_z$ with z being about 5.75. The oxygen content is designated by z since the exact stoichiometric proportion of oxygen in CSVO can vary depending on whether the cathode material is prepared in
25 an oxidizing atmosphere such as air or oxygen, or in an inert atmosphere such as argon, nitrogen and helium. For a more detailed description of this cathode active material reference is made to U.S. Patent Nos. 5,472,810 to Takeuchi et al. and 5,516,340 to Takeuchi et al., both
30 of which are assigned to the assignee of the present invention and incorporated herein by reference.

One exemplary sandwich cathode electrode has the following configuration:

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102750 : 0556580

SVO/current collector/CF_x/current collector/SVO

Another exemplary sandwich cathode electrode configuration is:

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SVO/current collector/SVO/CF_x/SVO/current collector/SVO

Still another configuration for an electrochemical cell with a sandwich electrode has a lithium anode and a cathode configuration of:

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SVO/current collector/CF_x, with the SVO facing the lithium anode.

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CG3 In a broader sense, it is contemplated by the scope of the present invention that the second active material of the sandwich cathode design is any material which has a relatively lower energy density but a relatively higher rate capability than the first active material. In that respect, other than silver vanadium oxide and copper silver vanadium oxide, V₂O₅, MnO₂, LiCoO₂, LiNiO₂, LiMn₂O₄, TiS₂, Cu₂S, FeS, FeS₂, CuO₂, copper vanadium oxide (CVO), and mixtures thereof are useful as the second active material.

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Before fabrication into a sandwich electrode for incorporation into an electrochemical cell according to the present invention, the first and second cathode active materials prepared as described above are preferably mixed with a binder material such as a powdered fluoro-polymer, more preferably powdered polytetrafluoroethylene or powdered polyvinylidene fluoride present at about 1 to about 5 weight percent of the cathode mixture. Further, up to about 10 weight

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percent of a conductive diluent is preferably added to the cathode mixture to improve conductivity. Suitable materials for this purpose include acetylene black, carbon black and/or graphite or a metallic powder such as powdered nickel, aluminum, titanium and stainless steel. The preferred cathode active mixture thus includes a powdered fluoro-polymer binder present at about 3 weight percent, a conductive diluent present at about 3 weight percent and about 94 weight percent of the cathode active material.

A second embodiment of a present invention cell is constructed according to U.S. Patent No. 5,639,577 to Takeuchi et al. This patent describes a cathode active blend of fluorinated carbon and a transition metal oxide. By blending is meant that the already prepared active materials of CF_x and CSVO are comingled together in a relatively homogeneous mixture. Again, the fluorinated carbon is prepared from the carbonaceous precursors described above. According to this patent, the preferred transition metal oxide is CSVO. However, other active materials including SVO as described above with respect to the second cathode active material of the sandwich electrode design are also useful when blended with CF_x . This cell is described as being particularly useful for high current pulse discharge applications, for example at about 15.0 mA/cm² and above.

Cathode components for incorporation into an electrochemical cell according to the present invention may be prepared by rolling, spreading or pressing the first and second cathode active materials onto a suitable current collector selected from the group consisting of stainless steel, titanium, tantalum, platinum, gold, aluminum, cobalt nickel alloys, nickel-containing alloys,

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highly alloyed ferritic stainless steel containing molybdenum and chromium, and nickel-, chromium- and molybdenum-containing alloys. The preferred current collector material is titanium, and most preferably the titanium cathode current collector has a thin layer of graphite/carbon material, iridium, iridium oxide or platinum applied thereto. Cathodes prepared as described above may be in the form of one or more plates operatively associated with at least one or more plates of anode material, or in the form of a strip wound with a corresponding strip of anode material in a structure similar to a "jellyroll".

In order to prevent internal short circuit conditions, the cathode is separated from the Group IA, IIA or IIIB anode by a suitable separator material. The separator is of electrically insulative material, and the separator material also is chemically unreactive with the anode and cathode active materials and both chemically unreactive with and insoluble in the electrolyte. In addition, the separator material has a degree of porosity sufficient to allow flow there through of the electrolyte during the electrochemical reaction of the cell. Illustrative separator materials include fabrics woven from fluoropolymeric fibers including polyvinylidene fluoride, polyethylenetetrafluoroethylene, and polyethylenechlorotrifluoroethylene used either alone or laminated with a fluoropolymeric microporous film, non-woven glass, polypropylene, polyethylene, glass fiber materials, ceramics, polytetrafluoroethylene membrane commercially available under the designation ZITEX (Chemplast Inc.), polypropylene membrane commercially available under the designation CELGARD (Celanese Plastic Company, Inc.) and a membrane commercially available

under the designation DEXIGLAS (C.H. Dexter, Div., Dexter Corp.).

5 The electrochemical cells of the present invention further include a nonaqueous, ionically conductive electrolyte which serves as a medium for migration of ions between the anode and the cathode electrodes during the electrochemical reactions of the cells. The electrochemical reaction at the electrodes involves conversion of ions in atomic or molecular forms which
10 migrate from the anode to the cathode. Thus, nonaqueous electrolytes suitable for the present invention are substantially inert to the anode and cathode materials, and they exhibit those physical properties necessary for ionic transport, namely, low viscosity, low surface
15 tension and wettability.

A suitable electrolyte has an inorganic, ionically conductive salt dissolved in a nonaqueous solvent, and more preferably, the electrolyte includes an ionizable alkali metal salt dissolved in a mixture of aprotic
20 organic solvents comprising a low viscosity solvent and a high permittivity solvent. The inorganic, ionically conductive salt serves as the vehicle for migration of the anode ions to intercalate or react with the cathode active material. Preferably, the ion forming alkali
25 metal salt is similar to the alkali metal comprising the anode.

In the case of an anode comprising lithium, the alkali metal salt of the electrolyte is a lithium based salt. Known lithium salts that are useful as a vehicle
30 for transport of alkali metal ions from the anode to the cathode include LiPF_6 , LiBF_4 , LiAsF_6 , LiSbF_6 , LiClO_4 , LiO_2 , LiAlCl_4 , LiGaCl_4 , $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiSCN ,

LiO₃SCF₃, LiC₆F₅SO₃, LiO₂CCF₃, LiSO₆F, LiB(C₆H₅)₄, LiCF₃SO₃, and mixtures thereof.

Low viscosity solvents useful with the present invention include esters, linear and cyclic ethers and
5 dialkyl carbonates such as tetrahydrofuran (THF), methyl acetate (MA), diglyme, triglyme, tetraglyme, dimethyl carbonate (DMC), 1,2-dimethoxyethane (DME),
1,2-diethoxyethane (DEE), 1-ethoxy,2-methoxyethane (EME), ethyl methyl carbonate, methyl propyl carbonate, ethyl
10 propyl carbonate, diethyl carbonate, dipropyl carbonate, and mixtures thereof, and high permittivity solvents include cyclic carbonates, cyclic esters and cyclic amides such as propylene carbonate (PC), ethylene carbonate (EC), butylene carbonate, acetonitrile,
15 dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, γ-valerolactone, γ-butyrolactone (GBL), N-methyl-pyrrolidinone (NMP), and mixtures thereof.

A preferred chemistry for a sandwich cathode electrode according to the present invention has a
20 lithium metal anode and a cathode electrode comprising (SVO) and fluorinated carbon (CF_x). In the sandwich structure, CF_x material is sandwiched between two cathode current collectors. This assembly is, in turn, sandwiched between two layers of SVO material. The
25 electrolyte activating the cells is 0.8M to 1.5M LiAsF₆ or LiPF₆ in a 1:1, by volume, mixture of propylene carbonate and 1,2-dimethoxyethane. Preferably, the electrolyte also contains 0.05M dibenzyl carbonate (DBC), as described in U.S. Patent Nos. 5,753,389 and 6,221,534,
30 both to Gan et al. and both assigned to the assignee of the present invention and incorporated herein by reference.

The following examples describe the manner and process of an electrochemical cell according to the present invention, and they set forth the best mode contemplated by the inventors of carrying out the invention, but they are not to be construed as limiting.

EXAMPLE I

Six test cells were constructed having lithium anode material pressed on a nickel current collector screen.

10 The cathodes used two layers of titanium current collector screen and had the sandwich configuration of: SVO/current collector/ CF_x /current collector/SVO. A prismatic cell stack assembly comprising two layers of microporous membrane polypropylene separator disposed

15 between the anode and cathode was prepared. The electrode assembly was then hermetically sealed in a stainless steel casing in a case negative configuration and activated with an electrolyte of 1.0M LiAsF_6 in a 50:50 mixture, by volume of PC and DME with 0.05M DBC

20 dissolved therein. The theoretical capacity of the cells was 2.645 Ah.

Two of the test cells were constructed having CF_x synthesized from petroleum coke (group 1) while four of the cells were constructed with CF_x synthesized from

25 carbon fiber (group 2). A representative cell from each of groups 1 and 2 was accelerated pulse discharged. This discharge regime consisted of pulse trains of four 10 second 2 Amp current pulses with a 15 second rest between each pulse. The pulse trains were applied every 30

30 minutes. The capacities delivered to three voltages cut-offs are summarized in Table 2.

Table 2

Group	Capacity at Cut Off (mAh)			Efficiency at Cut Off (%)		
	2.0V	1.7V	1.5V	2.0V	1.7V	1.5V
1	1816	2069	2274	68.7	78.2	86.0
2	1967	2205	2320	74.4	83.4	87.7

The data in Table 2 demonstrate that the representative group 2 cell having a sandwich cathode design with CF_x synthesized from carbon fiber delivered more discharge capacity at a higher efficiency than the representative group 1 cell having CF_x in a sandwich cathode design synthesized from petroleum coke to all three voltages cut offs.

EXAMPLE II

To demonstrate the swelling characteristics of the groups 1 and 2 cells, one cell from group 1 and three cells from group 2 were discharged in a similar manner as the cells in Example I except only 50% of the theoretical capacity was removed. Cell thickness was measured before and after this discharge test. Cell thickness was also measured before and after discharge of the cell of Example I. The thickness data from these tests is summarized in Fig. 9 where the group 1 cell, curve 40, swelled significantly. In fact, the larger the DOD, the greater the cell swelling. In contrast, the group 2 cells, curve 42, exhibited fairly insignificant swelling throughout discharge.

It is appreciated that various modifications to the inventive concepts described herein may be apparent to those skilled in the art without departing from the

spirit and scope of the present invention as defined by
the hereinafter appended claims.

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